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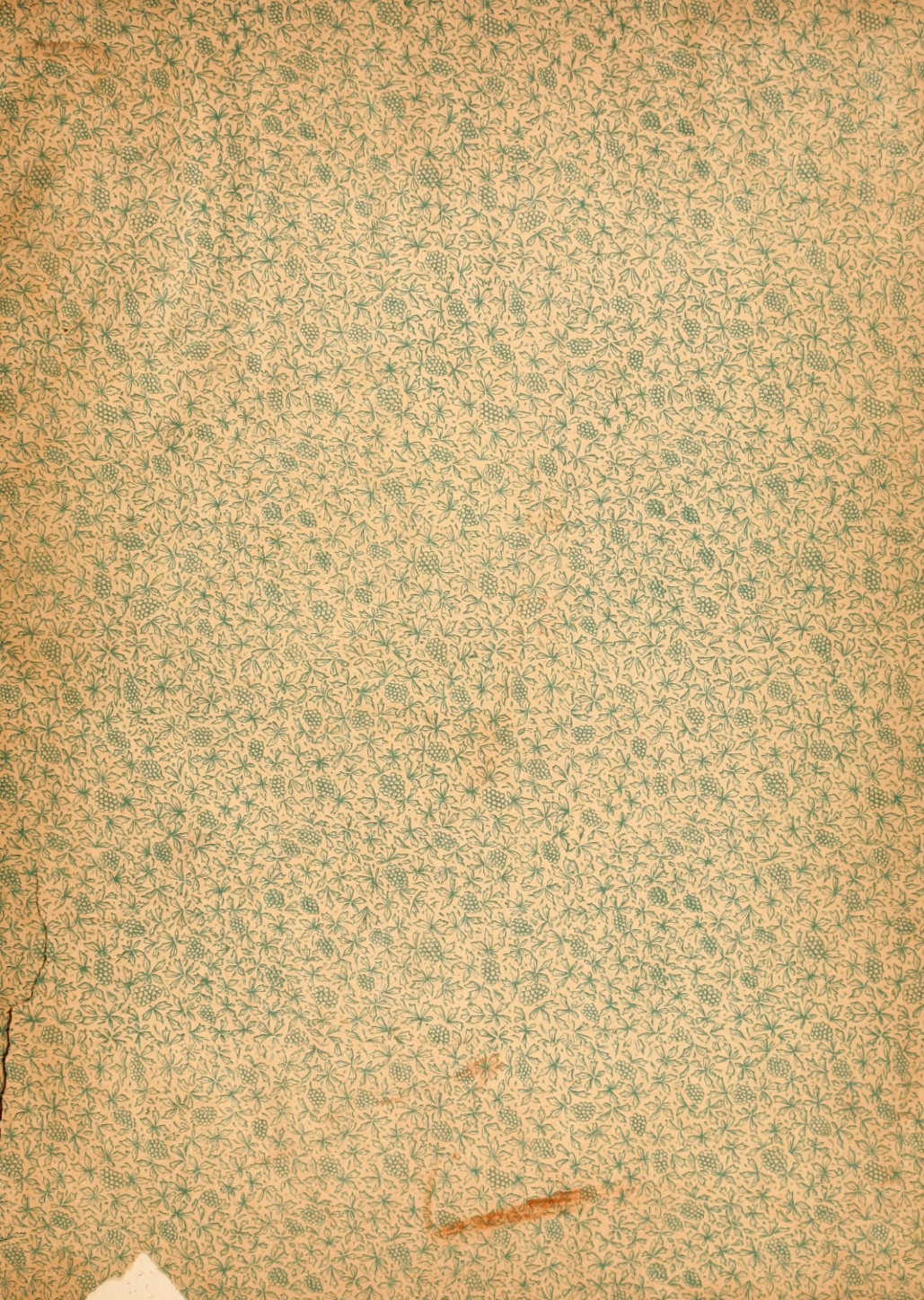
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Johns Hopkins University







The Action of Light
on some Organic Acids in the presence
of Uranium Salts.

Dissertation
submitted to the Board of University Studies
of The Johns Hopkins University
for the Degree of Doctor of Philosophy
by
Henry Fay -

1895

71.254

Acknowledgment.

The author wishes to express his deep sense of gratitude to Professor Hansen under whose guidance this work was carried on, and from whom he has received valuable instruction not only in the lecture room, but also in the laboratory, where his helpful suggestions and friendly interest have been words of encouragement.

He also wishes to express his appreciation of the instruction received from ¹⁰ Professor Hansen

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Historical.

The early history of photo-chemical reactions is connected with the history of photochemistry.

Shulze¹ in 1727 gave a demonstration that the darkening of silver salts was due to the action of light and in 1795 Berzelius² showed the effect of the different parts of the spectrum. It had been noticed some centuries before that silver salts were subject to change, but the work of Shulze was the first conclusive evidence that this change was due to the action of light. In the early part of this century the action of light on plant growth was studied by many investigators who received the incentive from a suggestion made by Priestley³.

Certain physical phenomena were early noticed in the early hours of investigation by Petit⁴, who showed in 1722 that solutions of potassium nitrate and magnesium chloride crystallized more readily in the sunlight than in the dark. These effects

1.

2. *Traité de l'air et du Feu*

3.

4. *Mémoires de l'Académie des Sciences*

were studied more fully by Chaptal¹ and Dize². In 1843

Bequerel³ began his excellent researches on the phosphorescence of the sulphides of barium, calcium and strontium, but none of these substances was in itself or the compounds of the metals sensitive to faint light. Photography was being developed in the early part of the century and was used to make plates but not plates from the mineral side. During this period many inorganic salts were found which undergo some change when exposed to the sunlight, and in general this change was a reduction, especially if there was an oxidizing or organic substance present.

Among the salts most extensively studied were the salts of uranium. Before taking up the study of the reactions connected with uranium salts we decomposed in the sunlight. It would be well to review the work which has been done on the organic substances which are subject to change when exposed to the light. Many observations have been recorded

1. Mém. de l'Acad. Roy. des. Sc. de Toulouse vol 3.; Journ. de Phys. 24.

2. Sur la cryphallisation etc. 1789.

3. Ann. Chim. Phys. [3] 9. 257

in which the fact is simply stated that certain substances are sensitive to light, but one, in a given case, has the reaction been a clean one. In the cases studied the reactions can be classified under one of these three classes - Substitution, Direct Combination, and Polymerization

Dumas¹ has shown that the hydrogenation of the methyl groups in acetic acid can be replaced by chlorine when the two substances are exposed to direct sunlight, giving a substituted acetic acid. Phenomena of a similar nature were brought out by Schramm² who noticed that when the aromatic hydrocarbons having a side chain were treated with chlorine in the direct sunlight the substitution always takes place in the side chain.

Under the second class come the researches of Calkins³ who showed that certain ethers of the methyl series can be formed when the alcohol and acid are brought together in the sunlight. Chastain⁴ expressed

1. Ann. Chem. Phys. [2] 73 77

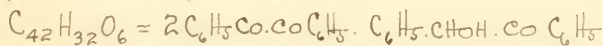
4. Ann. Chem. Phys. [5] 11 145.

2. Berichte. 18. 350, 606, 1272; 19. 212.

3. Comp. Rend. 23. 1070.

acetic and butyric acids with alcohol and by means of distillation was able to remove the acids by distillation.

Somewhat similar are the facts discovered by Klinger¹ who showed that aldehydes have the power of combining directly with phenanthrenequinone. He also noticed that if a reducible substance be exposed to the light in presence of an oxidizable one, the solvent is oxidized while the substance in solution is reduced. By this means Klinger was able to convert phenanthrenequinone into phenanthrenehydroquinone and at the same time the solvent, ether, was oxidized to acetic aldehyde. He found that benzil in ether solution passes over into a substance which he calls benzil-benzoin on account of the ease with which it can be broken down into these two substances. He represents the decomposition by the equation



Under the class of polymerization come the

just noticed by Sponner. He found that carbon and nitrogen were polymerized when exposed to the sunlight. Similar facts have been noticed in the field of inorganic chemistry, as in the case of phosphorus and arsenic.

The green phosphorus is converted into the red modification and a solution of white phosphorus in carbon bisulphide deposits the modification.

The work of Tyndall² on light reactions cannot be placed under any of these heads as the nature of the reactions is not known. He exposed the vapour of amyl nitrate to a beam of light and found that there was decomposition; oxides of nitrogen were formed but the other products were not examined. Tyndall also found that allyl and isobutyl iodides are affected by light, but he did not study the subject from its chemical side.

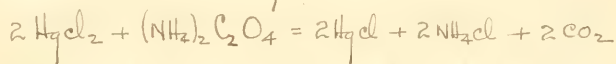
Oxalic acid has been extensively used in photochemical reactions, especially in form of its salts and it has been recommended as a means

1 Comp. Rend. 93 514.

2 Proc. Royal Society 17, 92-104.

of determining the amount of sunlight. Dubrunval¹ proposed to use ferrous oxalate as a photometer in which the ferrous oxalate or carbon dioxide given off could be measured. He also found that oxalic acid would reduce platinum chloride to metal and that silver oxide is partially reduced to metal.

Edwards² used as a photometer solution of ammonium oxalate and mercuric chloride which on exposure to sunlight gave off carbon dioxide and hydrochloric acid according to the equation



Having reviewed briefly the effects of light on certain organic substances, the history of the reactions which include the use of uranium salts will be given in detail. The first person to find that uranium salts were sensitive to light was Berzelius³ who described in 1825 certain effects produced by the sun's light and alcohol. He says: "Dissolve of uranium dioxide in 25 parts of alcohol and the solution undergoes remarkable changes on

1 Schweigger's source. 62, 90.

2 Ann. Chem. Phys. (2), 1825.

3 Ann. Min. Phys. [1] 56, 142.

exposed to the sun. The yellow liquid becomes turbid and deposits a grayish green substance. After several days exposure, the solution acquires an odour, intense ether; the filtrate is colorless and contains no uranium; the precipitate is of a green glass and retains sulphuric acid." Bruchatz further observed that an ether solution of uranyl nitrate becomes green on exposure to sunlight and a black substance is deposited. Chemists added little to these observations until Ebelman in 1831 took up the subject. He confirmed the results of Bruchatz with the sulphate of uranium and alcohol, but noticed in addition that green crystals were formed which he said were the protoxide of uranium. The precipitate he called the "bi basic sulphate of the protoxide" and gave it the formula $2UO_3 + 2H_2O$.

The oxide of uranium was also investigated by Ebelman. He observed that a solution of uranyl oxalate decomposes into a brown substance, which he believed to be the hydrated oxide, and into carbon dioxide and carbon monoxide in changing proportions.

St. Victor and Carus¹ working on the action of light on organic substances noticed that if a solution of oxalic acid be exposed to light a small quantity of carbonic acid is evolved. This heated to boiling, a gas is evolved from a solution of oxalic acid with a one percent solution of ammonium nitrate, finding that in the dark no decomposition would take place, but after exposure to the sun, light action soon began. They say that carbon monoxide was given off but do not mention the composition of carbon dioxide. As the gas is in fact decomposed by them, we think a more gradual exposure of ammonium nitrate increased toward the action of light on oxalic acid in the solution it was heated and glucose.

Zeckamp² repeated the work of St. Victor and Carus and found that after a solution of ammonium nitrate and oxalic acid had been exposed to the light for some time there was a deposit of a green crystalline powder, the solution became colorless and reacted acid. The acid was not changed to formic acid by means of lead and



barium salts. From succinic and he obtained carbon dioxide and propionic acid, and the precipitate which was formed he believed to be uranous succinate. Butyric acid and carbon dioxide were obtained from pyruvic acid.

H.C. Bolton in a review of the work done on uranium in photochemical reactions adds some interesting results. He found while working with certain uranium salts in photographic processes. He obtained a salt which is the double fluoride of uranium and potassium having the composition represented by the formula $2\text{UO}_2\text{F} + 3\text{KF}$.

A solution of this salt acidified with formic acid does upon in the sunlight forming a precipitate which Bolton gives the formula $4\text{UF} + \text{KF}$. Drabbe and agents a similar reduction, but with the formation of Ebelman's uranyl hydrate². Solutions of the nitrate, sulphate, oxychloride and oxyfluoride of uranium are reduced when mixed with glycerine and placed in the sunlight. Even in the dry state the uranium ammonium chloride was found to be sensitive

to light.

Wislar¹ next took up the study of light on uranium salts. He arranged reactions on pyruvic acid and showed in addition that butyric acid in presence of uranium salts breaks down into propane and carbon dioxide.

Some time similar to the work of Wislar, that of Lucien Bonaparte² who obtained carbon monoxide of valeric acid by exposing it with a solution of uranyl valerate. The products generated he believed to be uranium salts and gases which were not analyzed but believed to be carbon dioxide, carbon monoxide and a hydrocarbon.

Chastain³ studied the red and violet rays of the spectrum on solutions of uranyl nitrate and alcohol and noticed the odor of aldehyde which is probably the odor Bonaparte took for nitroaldehyde. Some uranyl salts were present in the solution.

At the suggestion of Professor Koenig H.C. goes working on the laboratory undertook the study of the action of light on uric acid in the presence of

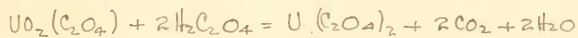
1. Ann. 262. 232.

2. Jour. Gouv. Prék. Chem. 30, 308.

3. Ann. Chim. Phys. [5]. 11, 145.

uranium salts. As his work has not been published a short account of his work will be given.

He verified the statement of Deekamp that in the presence of uranium oxalate, oxalic acid is broken down into carbon dioxide, carbon monoxide and formic acid. The equation given by Deekamp to express the reaction



Deekamp thought that the green precipitate was uranous oxalate of the composition $\text{U}(\text{C}_2\text{O}_4)_2 \cdot 6\text{H}_2\text{O}$. A series of experiments were made by Jones in which varying amounts of uranyl oxalate and oxalic acid were used and the amount of carbon dioxide formed in every case agreed to within a few c.c. with the amount of carbon dioxide which would have been liberated from the oxalic acid used. But it decomposed directly into carbon dioxide, carbon monoxide and water. The amount of carbon monoxide set free, plus the amount contained as gas in the air, was always constant.

less than the carbon dioxide.

The composition of the precipitate formed was found to depend on the amount of uranyl oxalate, relative to the oxalic acid, originally used. In all cases where a very large excess of oxalic acid was not used, it could be clearly seen that the precipitate was a mixture of crystals and an amorphous mass. Analyses of the precipitate formed from various mixtures confirmed the belief that the precipitate was a mixture. When a solution containing three grams of uranyl oxalate and thirty grams of oxalic acid had been exposed to the light for a time, it was noticed that green crystals were forming on the sides and bottom of the flask. The solution was then removed from the light and allowed to stand in diffused light for some time, when a considerable quantity of the crystals was obtained. An analysis of the crystals gave 45.05% uranium, which agreed fairly well with the composition $U(C_2O_4)_2 \cdot 6H_2O$ which contains 45.84% uranium.

A solution was prepared containing three grams uranyl

oxalate and forty-nine grams oxalic acid. Pure crystals were obtained, which contained 46.05% uranium. It thus appears that the crystalline compound is formed pure only when a very large excess of oxalic acid is used.

It was then hoped that by mixing a large amount of uranyl oxalate relative to oxalic acid, that the amorphous compound might be obtained in pure condition, but from the different mixtures used this did not prove unnecessary.

It was found further that a very small quantity of uranyl oxalate will decompose a very large quantity of unlimited amount of oxalic acid, if exposed continuously to direct sunlight & that continuously the crystalline compound will separate as long as the solution and the action will cease. Thus the reaction suggested by S. Kemp cannot express the whole truth, since in terms of it, one molecule of uranyl oxalate can decompose only five molecules of oxalic acid. The uranyl salt seems to act in some way as an oxidizing agent on the precipitate — at least as a product of the uranium salt used.

Decomposition of Oxalic Acid in presence of Ureyl Oxalate.

As the nature of the precipitate formed when oxalic acid is exposed to the sunlight in presence of ureyl oxalate was not completely settled by Jones I was decided, at Professor Remsen's suggestion, to continue the work and study the products of decomposition. For this purpose solutions containing oxalic acid in varying proportions were made and in all cases it was found that after a considerable time had been given over, the solutions became cloudy and then deposited a light green crystalline powder. When most of the oxalic acid was decomposed and the evolution of gas had ceased, there was deposited the remainder of the oxalic acid in solution as a globose, purplish brown substance. Finally, the concordant results could not be obtained by any longer with the green precipitate was obtained and I was decided to remove the light green coloured precipitate when first formed.

To obtain it 3 grams ureyl oxalate and 7 grams oxalic acid were dissolved in a little water and exposed to the direct sunlight. When morning the green

precipitate just formed had settled to the bottom of the flask, it was gathered up, washed with water and then dried between filter papers. The dry substance has a very pale green color, and showed no tendency to oxidation or change of any kind.

The uranium was determined by heating the substance in a porcelain crucible and weighing as the oxide U_3O_8 . In all of the analyses made this method was used; very often, however, the oxide just formed was converted into the nitrate, and the nitrate again changed into the oxide. This was done simply to control the results as the oxide U_3O_8 no more readily formed from the nitrate than from the uranium salt or organic acid. In analyzing the green nitric solution these results were obtained:

2.637 grams substance	gave	1.776 grams U_3O_8	= 57.17% U
2.015 " " "	"	1.369 " " "	= 57.68% U
2.560 " " "	"	1.725 " " "	= 57.20% U
Calculated for $U(C_2O_4)_2$			57.69% U

This shows the substance to be a monomer. It can be obtained at any time provided the solutions be continuously exposed to the sunlight and not too large an excess of acetic acid be present. It has been seen that when a large excess of acetic acid is present and the solutions removed after a short exposure to the light there is nothing tending to the formation of the crystalline product $U(CO_3)_2 \cdot 6H_2O$. As the solutions be exposed until all of the acetic acid is decomposed there is then formed some of the purplish brown substance.

Desiring to obtain the purplish brown precipitate in pure condition, several attempts were made to get it from solutions containing excess acid and attempt made by removing the water as it is formed and re-exposed to sunlight but in this case the precipitate contained a mixture of the eight year uranium acetate and the purplish brown substance. To get a pure precipitate in solution was exposed to the sunlight there is formed the same purplish brown

weight and then added gradually to the amount
of water gas obtaining it.

Decomposition of Wrenyl Oxalate.

Two grams wrenyl oxalate were dissolved in one
litre of water and the solution filtered to get rid of a small
amount of undissolved substance. The solution was exposed
to direct sunlight and within five minutes after exposure
the clear yellow solution had become cloudy. The cloudiness
increased rapidly. In half an hour there was a deposit on
the peripheral brown substance on the bottom and sides of
the glass nearest to the source of light. There was no
evolution of gas whatever. Thinking possibly the solution
may have held the gas, several attempts were made to
collect any gas formed by attaching large tubes of lead with
wrenyl oxalate solutions to retorts containing mercury
under much reduced pressure and even by gentle heating
it was impossible to collect any gas. The precipitate formed
in the above solution was filtered off, washed with water
and left to dry in the air. The brown substance on drying

changed to a yellowish, so that it was impossible to prepare it in the way gas analysis. Even on drying rapidly between filter papers, there was some change noticed. If the brown substance be allowed to stand in the flask in which it is precipitated, the same change takes place although not so rapidly - The filtrate was always neutral to litmus and contained nothing except traces of uranium which was thrown out on evaporation to small volume. It was impossible in any case to get the uranium precipitated entirely although the portion remaining in solution was extremely small in comparison with the whole amount of uranium present.

Determination of Uranium in the Brown Precipitate.

Some of the yellow precipitated substance was partially dried between filter papers, then removed to a porcelain boat and then dried in a stream of dry hydrogen at 100°. The substance prepared in this way, has a pale grayish green color, resembling somewhat uranic carbonate, and in

This condition is a very little bit, say 10 per cent, into the yellow substance. It was weighed rapidly, placed in a combustion tube and heated in a current of oxygen. When heated under these conditions, the substance begins to glow and the combustion spreads rapidly throughout the mass. After very few minutes the substance is changed into the oxide U_3O_8 . The boat was then withdrawn and weighed. The oxide obtained in this way is a pale olive green color and appeared to be perfectly pure. The uranium was determined in six separate experiments in this way with the following results:

'4768 grams gave '4407 grams U_3O_8 = 78.47% U

'2373 " " '2180 " " = 77.99

'1372 " " '1249 " " = 78.0

'1556 " " '1414 " " = 77.15

'1856 " " '1696 " " = 77.58

'1454 " " '1314 " " = 77.41

Average of six determinations 77.76%

These results it will be seen are pretty concordant but

good results and must be obtained by a better method. Attempts were made to determine the percentage of carbon, but the error it was involved in comparison with the large amount of uranium that concordant results could not be obtained. The substance when heated alone gives off a small amount of carbon monoxide, but even by passing the gases over glowing copper oxide it was impossible to determine the carbon with any degree of accuracy. Better results were obtained with the yellow substance into which the brown one passes. These will be taken up later -

Various attempts were made to isolate the acid contained in this salt without success. The substance dissolves readily in hydrochloric, sulphuric and nitric acids, forming green solutions from which ammonia precipitates uranous hydroxide. All that can be said at present in regard to this salt is that it is a reduction product of a complex salt. There can be no doubt that it contains a small percentage of carbon as will be made more evident when the yellow transuranic product is considered. Electron behavior

it to be hydrated oxide, but the presence of a brown powder
this assumption to be wrong. Baston obtained the same
precipitate by evaporating a solution of the soluble compounds
of uranium and potassium acidified with oxalic acid.
He however did not analyze the product nor was there
any comparison. If this were the simple hydrated oxide
I would think I should also be formed when the same salt as
Baston is acidified with formic acid. In this case only
the salt $4UF + KF$ is formed.

Analysis of the Yellow Substance obtained from the Purple-brown Precipitate.

The best way of preparing the yellow salt is to
allow the Brown substance to stand in a desiccator
for four or five days. It is also formed when allowed
to stand in the air, but it is more convenient to use
the desiccator as, in this way, the yellow salt can be
obtained in dry condition having constant weight. In
its analysis of the salt, I have dried it in the weight.

over sulphuric acid and by heating in a bulb to 100° .

The substance is also formed when the brown precipitate is allowed to stand under water gas several weeks. A gas analysis test was made for carbon by heating the substance in a tube through which pure air was drawn. The gases were passed into barium hydroxide solution, there was considerable barium carbonate formed, showing carbon to be present.

This substance was heated in a combustion tube as in the previous case and the uranium oxide was obtained thus determining the uranium, carbon and hydrogen in the same operations. The gas which it gave consisted of water, black red substance, probably U_2O_5 and CO_2 . By heating gave the oxide U_2O_5 .

Different preparations gave the following analyses

Uranium.	Carbon.	wt. %
75.46	1.36	8.58
75.40	1.02	8.04

75.10

1.2

8.5

74.9

1.15

8.7

75.44

—

—

Quite a number of analyses were made which are reported very clearly in the table given. The last three analyses of uranium given was very kindly made by Mr. H.C. Jones. The specimens of the substance which were used for analysis had been kept about seven months and was dried to constant weight in an air bath.

It is difficult to answer the question as to whether any carbon is present, but is none of the carbon was given off in the original decomposition and the Green substance does not lose any carbon dioxide on drying. It is very likely that all the carbon was in combination with the uranium. In what form it exists it is difficult to say, as the substance dissolves in acids with the exception of any organic acid. To cause the uranium to be precipitated and the gas to be evaporated, there is no evidence of any organic substance remaining behind. This is the

a satisfactory formula has not been found to represent the reaction or the percentages found.

Formation of Formic Acid in the Decomposition of Oxalic Acid.

Gouss has shown in his work that the equation of DeLong representing the decomposition of oxalic acid by a metal oxide, does not agree with the reaction as it does not account for the formic acid found, nor for the carbon monoxide. It was thought advisable to make a few experiments to see if the formic acid can be built up from carbon monoxide and water in presence of a vacuum seal. For this purpose the following experiments were made

I. A 250 cc Erlenmeyer flask was filled with water and its solution, and then the air was exhausted. It about 100 cc carbon monoxide. The inverted flask was connected with a long tube bent twice at right angles to draw pressure. The flask was placed in the light sunlight. After

to have the loss of the acid and water
and the gas up to the same as the
original mixture was to be decomposed. The gas
was detected in the solution.

II Carbon monoxide and water were exposed for
eight days to the direct sunlight. At the end
of this time the water was perfectly neutral.

III. Mixtures of equal volumes of carbon monoxide
and carbon dioxide in the presence of water were exposed to
the direct sunlight but without obtaining any formic acid.

From these experiments it is shown that the formic
acid found in the decomposition of oxalic acid is from the
oxalic acid itself, and not from the combination of
carbon monoxide and water.

Decomposition of Malonic Acid

The study of malonic acid was next taken up and it was
intended to proceed down the acid to malic acid but was not

dry culture arose.

Triethyl malonate was prepared by bringing together hot concentrated solution of malonic acid and urea and initiate it rapidly in a few moments as a bright, fine crystalline powder collecting primarily to the sides of the beaker. It is readily suspended in water and alcohol, more readily soluble in dilute acids, and easily soluble in a solution of malonic acid. On analysis it gave the following results for uranium

2.526 grams gave 1.656 grams U_3O_8 = 55.65% U.

3.682 " " 2.416 " " = 55.70% U.

Heated to 110° for 3 hours it lost 9.15% H_2O

Calculated for $2H_2O$ 8.78%

At 180° 2.670 grams lost in weight .0325 grams = 12.16% H_2O

Calculated for $3H_2O$ = 12.6%

Calculated for $CH_2(COO)_2 \cdot UO_2 \cdot 3H_2O$ = 56.06% uranium

This like many uranyl salts decomposes with heating, but loses the last water only at high temperatures.

As this salt is almost insoluble in water, it could

not be used for any decomposition. Usually, if a solution of uranyl nitrate and malonic acid was exposed to the light for a few minutes the uranyl malonate was completely precipitated. The uranyl malonate dissolves in potassium malonate and it was hoped to make such a solution for the decomposition. The double salt of potassium and uranium was made by dissolving the uranyl malonate in the required amount of potassium malonate. On evaporation white crystals but more or less bright yellow precipitates were obtained.

Solutions of the double salt and solution of malonic acid were exposed to the sunlight for several days, but there was no indication of decomposition in either case. They seemed to be perfectly stable in the bright^{est} sunlight. Negative results were also obtained when uranyl malonate was dissolved in malonic acid. — The malonic acid will decompose, however, when a dilute solution of uranyl malonate and malonic acid is exposed to the sunlight but the rate of decomposition is so extremely slow that it was not considered advisable to make the work further at the time.

Decomposition of Succinic Acid.

Attempts were made to decompose succinic acid by means of uranium succinate, but so far it has been impossible to effect such decomposition.

Uranium succinate is described in Watts' Dictionary as being made from uranium nitrate and acid sodium succinate by evaporation to dryness. This method was tried but the uranium salt obtained was so nearly insoluble in water that it was not suited for the experiments. Some of the salt obtained was however soluble in water as succinic acid and this solution exposed to the direct sunlight for some days showed no tendency to change. Various other methods were tried to obtain the uranium succinate, but they were not successful. Solutions of uranium nitrate and succinic acid can be evaporated to dryness in water bath or by the use of a water bath. It was also hoped to get it from barium succinate or uranium sulphate. These salts were brought together in molecular proportions but perhaps the barium was changed to sulphate and put into the insoluble barium uranate.

As it was desired to obtain the decomposition of succinic acid by means of uranium, the experiment was carried no further.

Duncan found that succinic acid decomposes in the sunlight in presence of uranium salts and carbon dioxide and propionic acid. This was carried qualitatively. The action takes place slowly and as this was continuing for some time during the summer months, the reaction was not carried further. Duncan believed the green precipitate formed in this case to be uranous succinate. A small amount of this substance was obtained and analyzed for uranium, but the percentage did not agree with that required for uranous succinate.

It seems necessary to do much more work on the precipitates obtained in these decompositions as this is difficult to obtain in pure condition and from analyses makes precipitates from other acids they do not seem to be the simple reduction product.

This is also found to be the case with tartaric acid.

Tartaric Acid.

When tartaric acid and ammonium nitrate are exposed to the sunlight, the ammonium nitrate gradually turns to a deep green color and after some time there is a precipitation of a light green solid matter. There is no green color in the reaction. Several experiments were attached to microscopes containing mercury, but there was no change in the color, although the solutions were under much reduced pressure. Next to this the precipitation was greatly reduced. When the green solution from which the precipitate had been removed was placed in a test-tube within there was complete precipitation. The most favorable conditions for obtaining the precipitate is when one mole of ammonium nitrate is exposed with one mole of tartaric acid. In the solution in which the precipitate has been formed, tartaric acid in the sunlight gradually converts the green solid salt into solution, forming an amber colored liquid. This is the green salt which is the product of the paper and the other acid tartaric product. Upon the

following results:-

'2631 g. am. g. '1667 g. am. U_3O_8

'2949 " " '1713 " U_3O_8

'2631 " " '0.555 " H.

'2949 " " '0.684 " H.

'2631 " " '1.396 CO_2

'2949 " " '1.662 " CO_2

Calculated for $U_6H_{12}O_{10}$ — Found

H.. 2.48% III. 2.34 IV. 2.57

C 14.87% VI. 15.3 V. 14.46

U 49.58% I, 49.3 II, 49.31

The nature of this precipitate cannot be ascertained from the above results and the formula suggested has no weighing basis at present. It may be possible to initiate the aqueous solution of the above salt but until this is done it cannot be able to speculate in regard to the nature of the precipitate.

Decomposition of Isobutyric Acid.

Whitaker has indicated the action of sunlight on butyric acid in the presence of ammonium salts and found that it decomposed into propane and carbon dioxide. He also thought isobutyric acid was similar to the other acids of this series and would undergo decomposition and a study was made accordingly of isobutyric, propionic, and acetic acids. The study of isobutyric acid was taken up first as it was found to work rapidly giving a good yield when exposed to the sunlight with acetyl nitrate.

Experiments were first made to see whether any change in solution existed between the whole mass of the green given rays.

Carbon dioxide was known to be present by its ready absorption by potassium hydride and the residual gas was burnt from the capillary tube of the nitrometer in which it was collected. It burned with a smoky flame which indicated it being a hydrocarbon. It was believed that the isobutyric acid would decompose in the same way as the butyric acid giving equal volumes of propane and carbon dioxide. This was found to be the case and is shown in the following experiments.

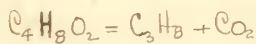
I. For the purpose of collecting the gas, the soil tubes were exposed in vacuum test tubes, 18 x 120 mm., connected by means of a capillary tube to a nitrometer filled with mercury. The acid to be used was poured directly into the tube and a weighed portion of oxygenate substrate was added. Water was now added to bring the water to the required height in the tube.

2.0201 grams of acetic acid and .3364 gram oxygenate substrate was dissolved in 30 c.c. of water and exposed to the sunlight. Gas begins to be given off about fifteen minutes after the exposure is made. After being exposed for nearly an hour the lower half of the solution becomes cloudy and there soon appear some deep green, wispy, lipid which gradually collects in the bottom of the test tube. Next, the gas evolved seems to come from this large drop. This dark green, waxy lipid no longer collects in a globular form and it disappears completely which has not yet been observed. Then a large foam formed a precipitate however as the the liquid are slight green powder.

The exposure was continued for several days with

all action ceased. All of the uranium was precipitated

The total volume of gas was 30 c.c. and of this 14.8 c.c. were absorbed by caustic potash which was the volume of gas to be carbon dioxide. It was shown that the time for reaction which had taken place was approximately 30% of the total amount calculated on the assumption that the reaction takes place through



at the end of the first day, approximately 20% of the time, portion had taken place.

II. This experiment went precisely as the preceding except that after the reaction had begun a tube is put with one end in a beaker around the tube containing the solution. This increased the velocity of the reaction very much and it was found that by this method, large quantities of the gas can be collected in a very short time. Of 4700 c.c. collected 13.6 c.c. were absorbed by caustic potash.

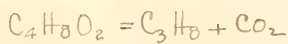
III. In this experiment much larger quantities of gas were collected and was used for the purpose of the hypercarbon gas analysis. After 25 c.c. of gas had been

collected it was covered from the nitrometer, was sealed and a pump glass, supplied with nitrogen, which was then broken in solution by the water used. This was repeated several times before the water was added, and the water was added at the end of the hydrocarbon.

The volume of the gas was made by having the gas under pressure by means of the pressure tube connected with the nitrometer, and then opening the gas stop-cock of the nitrometer only a little way. The stop-cock was closed before use, as the gas had escaped, thus making sure that no air could enter. By this means it was found possible to make the several gases, as that, on absorption and the change, the volume was shown to be smaller. The remaining portion was then transferred to the eudiometer and exploded with oxygen.

Volume of original gas	21.3 mm = 1 volume
Volume of solution of oxygen	400.7 mm = 18.81 volumes
Volume after explosion	335.9 mm = 15.76 volumes
Contraction	= 305 volumes

The calculated constitution for propionic $C_3H_7O_2$ is 3 volumes of gas over the hydrogen base to be prepared and the reaction is to be represented by the equation



Decomposition of Propionic Acid.

Propionic acid and anhydride are to decompose under certain conditions exposed to the sunlight giving off gas in a few minutes after exposure is made. It was found best to use a water solution rather than of the acid. The gas was passed over water and carbonic acid is thereby being rid of the acid is decomposed. The gas was collected and analyzed in the same manner as described under acetic acid.

I. 36.4 cc. of gas gave 15.8 cc. CO_2

II. 30.5 " " " 15.1 " "

III. 26.7 " " " 13.2 " "

These figures show that approximately 1/2 of the volume of the gas is carbon dioxide.

The mixture of the gases, with a contraction, was exploded with oxygen.

Volume of original gas — 19.97 m.m. = 1 volume

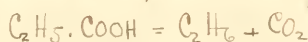
Volume after addition of oxygen 201.12 m.m. = 10.07 volumes

Volume after explosion — 147.44 m.m. = 7.38 volumes

Contraction — 2.69 volumes

Contraction calculated for ethane, C_2H_6 = 2.5 volumes

This proves the hydrocarbon to be ethane and the decomposition of propionic acid will be represented by the equation.



Decomposition of Acetic Acid.

Various attempts were made to decompose acetic acid in the same manner as propionic and isobutyric acids, but it was found to be successful only with the latter. The only preparation which were found to give azogas was when 15 c.c. glacial acetic acid and 5 c.c. strong solution of uranyl acetate were exposed. From this acid the gas was given off.

April and May taking about six weeks to collect enough gas analysis. The clear yellow solution did not change to its green color, so characteristic in all other cases, benzene. The mixture was not green, but it was not black.

Analysis of gas:—

13.4 c.c. of gas gave

6.4 c.c. CO_2

The remaining gas was run into a eudiometer and exploded with oxygen.

Volume of original gas

13.2 n.m. = 1 volume

Volume after addition of oxygen

108.24 n.m. = 8.2 volumes

Volume after explosion

80.52 n.m. = 6.1 volumes

Contraction

= 2.1 volumes

Calculated contraction gas methane, CH_4 , is 2 volumes while that found is 2.1 volumes which shows the gas to be methane and the decomposition is to be represented by the equation



It is in fact to note that the power of decomposition increases with water acid which breaks down under the

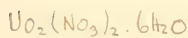
by light only, with difficulty. The process is apparently not
inorganic acid and it is therefore impossible to expect
any decomposition of this acid by light in the presence of
any substance.

Comparison of the Rates of Decomposition of Propionic, Butyric and isobutyric Acids

For the purpose of comparing the relative rates
of decomposition of these three acids, best normal conditions
were made by using not varying amounts of the substance
expressed with varying amounts of acid and initial. It was
decided to use propionic acid as the standard in
determining the best conditions possible.

The following table shows the comparison
between two solutions of propionic acid prepared
under exactly similar conditions. Solution #1
contains 10 cc. $\frac{1}{10}$ N $\text{CO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 10 cc. $\frac{1}{10}$ N propionic acid

Solution #2 contains 150.0 g/10 N propionic acid and 50.0 g/10 N



Hours of Exposure	Amount of Gas Collected.		Condition of Weather.
	#1	#2	
2	.8	.6	Clear
2 1/2	2.8	2.8	"
"	3.4	4.1	"
"	4.1	7.2	"
15	4.3	9.2	"

It will be seen that the solution containing the larger amount of acid acted the more rapidly. The exposure must exactly agree with the precipitate which is formed some time after the decomposition begins. The same point is well shown in the following table which is a comparison of the action

of propionic, isobutyric and butyric acids. Each solution contains 15 c.c. $\frac{1}{10}$ N acid and 5 c.c. $\frac{1}{10}$ N $\text{UO}_2(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$.

Number of days -

Amount of Gas Collected

	Propionic	Isobutyric	Butyric
1.	1.2	1.4	1.0
2.	2.5	3.0	2.5
3.	4.0	4.7	3.6
4.	5.3	5.7	4.3
5.	5.3	5.7	4.3
6.	6.5	6.4	4.9
10.	7.6	7.4	5.3
11.	8.8	8.4	—
12.	10.2	9.5	—
13.	12.0	10.6	9.0
14.	13.6	11.4	9.5
15.	15.0	12.4	10.5
16.	15.6	12.6	11.6
17.	16.3	13.0	11.7

It was found that on the next day the reaction gave
a white precipitate from the potassium acid and the malic acid was
practically the same. After this time there was no further change
in the solution, but after three days some there was
a precipitate in the solution containing malic acid
which was the same as the precipitate in the potassium
malate. The subject was dropped at this point, but it is
believed that interesting results can be obtained by working
during the summer months.

Conclusions.

It has been shown that the precipitate in the solution of oxalic
acid and malic acid, is formed in two stages; (1) formation
of oxalic acid; (2) formation of the purplish brown
precipitate from the oxalic acid in solution. The nature
of the latter has not been made up, but it is a complex
compound and is probably formed by the hydrolysis of
oxalic acid. The formation of the precipitate must
come from the oxalic acid itself as all
the other things in the solution are in excess.

presence of uranium salts has failed.

Tartaric acid when exposed with uranium salts to the light ~~is not~~ ^{is} insoluble precipitate with ~~insoluble~~ ^{insoluble} the nature of which has not been cleared up.

It has been shown that tartaric, pyruvic and carbonic acids decompose under the influence of corresponding to the acids and into carbon dioxide.

Biographical.

This author was born at Millersburg, Pennsylvania January 12, 1868. His early education was received in the public and private schools of Millersburg, Penn. In 1885 he entered Berea College and received the degree of Bachelor of Arts in 1889 and the degree of Master of Arts in 1892. He went to the Johns Hopkins University in October 1890. In February 1893 he left to accept a position in the department of the Pennsylvania Rail Road Company at Millersburg, but returned to the University in the fall of the same year. He was appointed lecture assistant to Professor Remond in October 1893 and has held the position two years.



